Thermal Degradation of Polyurethanes by Hexamethyldisilazane: Syntheses of Polyhexamethyleneurea with Organosilicon Reagents

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Synopsis

Representative aliphatic and aromatic polyurethanes undergo degradation upon treatment with hexamethyldisilazane (HMDS) at elevated teperatures. The course of the reaction is dependent on the nature of the polyurethane. Thus heating poly-[ethylene methylene bis(4-phenylcarbamate)] with HMDS in a sealed tube at 197°C gives high yields of 4,4′-diaminodiphenylmethane, trimethylisocyanatosilane, and 1,2-bis(trimethylsiloxyethane) along with lesser amounts of hexamethyldisiloxane, bis-(trimethylsilyl)carbodiimide, and ammonia. Under the same conditions, poly(ethylene N,N'-hexamethylenedicarboxylate) gives no diamine, but good yields of polyhexamethyleneurea and 1,2-bis(trimethylsiloxy)ethane together with smaller quantities of the other named products are obtained. In the course of this study, two novel routes to polyalkyleneureas were developed. For example, polyhexamethyleneurea is obtained in good yield by treatment of 1,6-hexanediamine with trimethylisocyanatosilane at elevated temperatures in a sealed tube. The reaction of 1,1′-hexamethylenediurea with HMDS under these conditions results in formation of the same product. A mechanism rationalizing the foregoing results is proposed which involves initial nucleophilic attack by HMDS on the polyurethane to give an intermediate disilylated urea. Thermal decomposition of this intermediate by alternative routes would give the observed products.
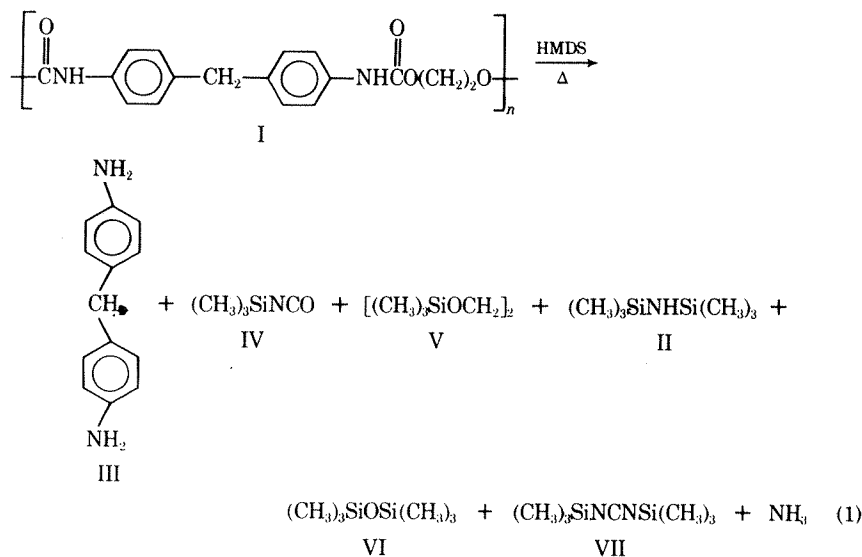
INTRODUCTION

There are numerous accounts in the chemical literature dealing with the thermal degradation of polyurethanes.[1-7] Monomeric urethanes are reported to undergo N-silylation in the presence of trimethylchlorosilane and triethylamine. Upon heating the silyl derivatives, thermal degradation gave the corresponding isocyanate and silyl ether in high yield.[8] Although successful with monomeric urethanes, all efforts to extend this method to polyurethanes failed. Recently we reported a new method employing hexamethyldisilazane (HMDS) (II)[9,10] for the thermal degradation of representative aromatic and aliphatic polyurethanes, poly[ethylene methylene bis(4-phenyl carbamate)] (I) and poly(ethylene N,N'-hexamethylenediamine dicarboxylate) (VIII). In these cases the course of the reaction depends on whether the N-aryl or N-alkyl substituted polyurethane is degraded. Treatment of the aromatic polyurethane I with HMDS gives only monomeric products. In contrast, the aliphatic polyurethane VIII affords as principal product a polyurea in high yield.

Consideration of the probable mechanistic course of the foregoing degradation of polyurethanes has led to the development of two novel and convenient synthetic routes to polyalkylureas, also involving the use of organosilicon reagents. As an example of the first method, 1,6-hexanediamine (XI) was heated with trimethylisocyanatosilane (IV); in the second, the 1,1′-hexamethylenediurea (XII) was heated with HMDS. In either case a good yield of the corresponding polyhexamethyleneurea (IX) was obtained.
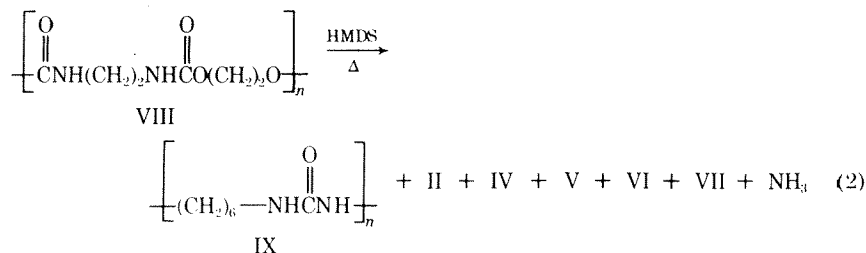
RESULTS AND DISCUSSION

Degradation of Polyurethanes

When poly[ethylene methylene bis(4-phenylcarbamate)] (I) was allowed to react with HMDS (II) at 197°C in a sealed tube, 4,4′-diaminodiphenylmethane (III), trimethylisocyanatosilane (IV) 1,2-bis(trimethylsiloxy)ethane (V), hexamethyldisiloxane (VI), and bis(trimethylsilyl)carbodiimide (VII) were produced [eq. (1)].

$$\left[\overset{\overset{\displaystyle O}{\|}}{\underset{}{-\text{CNH}}} - \bigcirc - \text{CH}_2 - \bigcirc - \text{NH} \overset{\overset{\displaystyle O}{\|}}{\underset{}{\text{CO}}} (\text{CH}_2)_2 \text{O} \right]_n \xrightarrow[\Delta]{\text{HMDS}}$$

I

$$\text{(III)} \quad + \quad (\text{CH}_3)_3\text{SiNCO} \quad + \quad [(\text{CH}_3)_3\text{SiOCH}_2]_2 \quad + \quad (\text{CH}_3)_3\text{SiNHSi}(\text{CH}_3)_3 \quad +$$
$$\qquad\qquad\qquad\qquad \text{IV} \qquad\qquad\qquad \text{V} \qquad\qquad\qquad\qquad \text{II}$$

$$(\text{CH}_3)_3\text{SiOSi}(\text{CH}_3)_3 \quad + \quad (\text{CH}_3)_3\text{SiNCNSi}(\text{CH}_3)_3 \quad + \quad \text{NH}_3 \quad (1)$$
$$\qquad\quad \text{VI} \qquad\qquad\qquad\qquad \text{VII}$$

However, when poly(ethylene N,N'-hexamethylenediamine dicarboxylate) (VIII) was subjected to the same conditions used with polyurethane I, polyhexamethyleneurea (IX) and compounds IV–VII were isolated [eq. (2)]. The identity of polyurea IX was unequivocally established by comparison with an authentic sample.[11]

$$\left[\overset{\overset{\displaystyle O}{\|}}{\underset{}{-\text{CNH}}}(\text{CH}_2)_2\text{NH}\overset{\overset{\displaystyle O}{\|}}{\underset{}{\text{CO}}}(\text{CH}_2)_2\text{O} \right]_n \xrightarrow[\Delta]{\text{HMDS}}$$

VIII

$$\left[-(\text{CH}_2)_6 - \text{NH}\overset{\overset{\displaystyle O}{\|}}{\underset{}{\text{C}}}\text{NH} \right]_n \quad + \quad \text{II} \; + \; \text{IV} \; + \; \text{V} \; + \; \text{VI} \; + \; \text{VII} \; + \; \text{NH}_3 \quad (2)$$

IX

It is interesting to note that other investigators have reported the formation of different types of products from pyrolysis of VIII and of poly-[ethylene tolylene-2,4-dicarbamate]. These differences were ascribed to a change in decomposition mechanism which was dependent on the electron-donating characteristics of the substituents.[4,5]
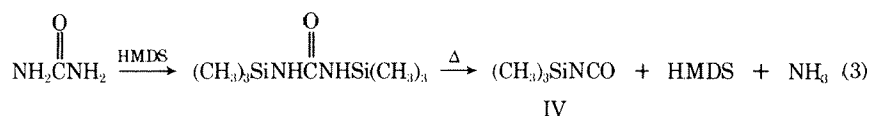
Mechanism of Degradation

The initial cleavage of either polyurethane I or VIII may be envisioned as involving nucleophilic attack by HMDS on the urethane moiety to give rise to 1,2-bis(trimethylsiloxy)ethane (V) and disilylated urea intermediate (X). Although weakly nucleophilic, HMDS has been reported[12] to convert urea to give N,N'-bis(trimethylsilyl)urea in a manner similar to that proposed by us in Scheme 1.
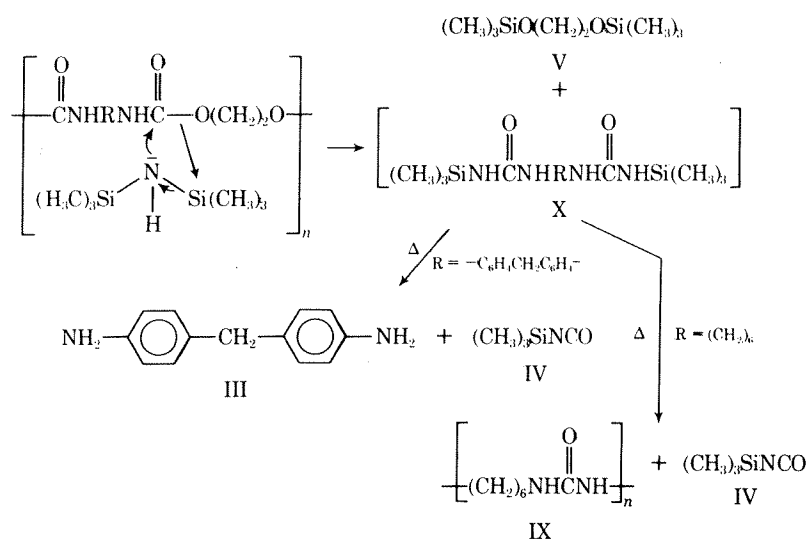
Scheme 1

This reaction is probably favored in the case of a polyurethane because of formation of the thermodynamically stable Si-O bonds of the 1,2-bis-(trimethylsiloxy)ethane (V).

$$NH_2\overset{O}{\overset{\|}{C}}NH_2 \xrightarrow{HMDS} (CH_3)_3SiNH\overset{O}{\overset{\|}{C}}NHSi(CH_3)_3 \xrightarrow{\Delta} (CH_3)_3SiNCO + HMDS + NH_3 \quad (3)$$
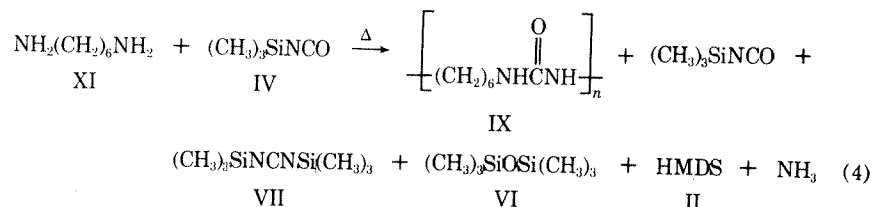$$IV$$

The thermal decomposition of the proposed intermediate may then occur in a manner similar to that of bis(trimethylsilyl) urea, which is reported to give IV, HMDS, and ammonia[7] [eq.(3)]. However, the decomposition of X can conceivably take the alternate course indicated in Scheme I, depending on the nature of the substituent R. Electron-withdrawing groups, such as aryl, would be expected to favor cleavage of the adjacent carbon-nitrogen bond leading to the formation of the corresponding diamine and IV. In support of this view, the thermal decomposition of intermediate X [R = $(C_6H_4)_2CH_2$] should give 4,4'-diaminodiphenylmethane (III) and trimethyl-
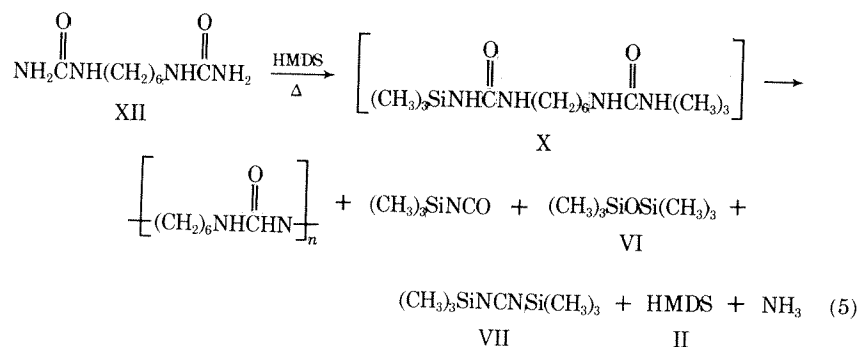
isocyanatosilane (IV). Since arylamines have been reported not to react with trimethylisocyanatosilane (IV), III and IV would not be expected to react under similar conditions. The presence of bis(trimethylsilyl)carbodiimide (VII) and hexamethyldisiloxane (VI) apparently results from the action of HMDS on IV. In this connection, it is noteworthy that compounds VI and VII were formed in low yield when trimethylisocyanatosilane (IV) was heated in a sealed tube with HMDS.

Polyurea Synthesis

The production of polyurea IX but not of 1,6-hexanediamine (XI) from the reaction of HMDS with polyurethane VIII suggested that the proposed intermediate X, R = $(CH_2)_6$, might have undergone thermal polymerization with concomitant expulsion of trimethylisocyanatosilane (IV). Support for the formation of polyhexamethyleneurea (IX) in this manner was provided by the reaction of trimethylisocyanatosilane (IV) with 1,6-hexanediamine (XI) in a sealed tube at elevated temperature. Polyurea IX was isolated in quantitative yield together with compounds II, IV, VI, and VII [eq. (4)].

$$
NH_2(CH_2)_6NH_2 \; + \; (CH_3)_3SiNCO \; \xrightarrow{\Delta} \; \left[\underset{(CH_2)_6NHCNH}{\overset{\overset{O}{\|}}{}} \right]_n \; + \; (CH_3)_3SiNCO \; +
$$

$$
\underset{XI}{} \qquad \underset{IV}{} \qquad \underset{IX}{}
$$

$$
(CH_3)_3SiNCNSi(CH_3)_3 \; + \; (CH_3)_3SiOSi(CH_3)_3 \; + \; HMDS \; + \; NH_3 \quad (4)
$$

$$
\underset{VII}{} \qquad\qquad \underset{VI}{} \qquad\qquad \underset{II}{}
$$

An alternative route to polyurea IX consisted in the treatment of 1,1'-hexamethylenediurea (XII) with HMDS in a sealed tube [eq. (5)].

$$
\underset{XII}{NH_2\overset{\overset{O}{\|}}{C}NH(CH_2)_6NH\overset{\overset{O}{\|}}{C}NH_2} \; \xrightarrow[\Delta]{HMDS} \; \left[(CH_3)_3SiNH\overset{\overset{O}{\|}}{C}NH(CH_2)_6NH\overset{\overset{O}{\|}}{C}NH(CH_3)_3 \right] \; \longrightarrow
$$

$$
\underset{X}{}
$$

$$
\left[\underset{(CH_2)_6NHCHN}{\overset{\overset{O}{\|}}{}} \right]_n \; + \; (CH_3)_3SiNCO \; + \; (CH_3)_3SiOSi(CH_3)_3 \; +
$$

$$
\underset{VI}{}
$$

$$
(CH_3)_3SiNCNSi(CH_3)_3 \; + \; HMDS \; + \; NH_3 \quad (5)
$$

$$
\underset{VII}{} \qquad\qquad \underset{II}{}
$$

Under these conditions X could not be isolated, but polyurea IX was produced in good yield, along with the expected degradation products, II, IV, VI, VII, and ammonia. Since the proposed intermediate X could not be isolated from any of the above reactions, it seems likely that under the reaction conditions, it is rapidly converted into the observed products. In each case X is the most probable initial product from the reaction of the organosilicon reagent with the substrate. The conversion of urea to

bis(trimethylsilyl) urea and its subsequent thermal degradation to compounds IV, II, and ammonia [eq. (3)] is consistent with such a view.

The possibility that diurea XII in the absence of HMDS might be the source of polyurea IX was also examined. Sealed tubes containing 1,1'-hexamethylenediurea (XII) were heated to 175°C and to 206°C (the melting point of XII) for 17 hr. The polymeric products obtained at both temperatures were identical and differed significantly from polyurea IX in thermal (DTA) and spectral (infrared) properties. These observations indicate that polyurea IX is not formed directly by thermolysis of XII and that the latter compound is not likely an immediate precursor of the polyurea.

EXPERIMENTAL

All starting materials, except where otherwise indicated, were obtained from commercial sources and were used without further purification.

A Hewlett-Packard Model 5750 chromatograph equipped with dual detectors (TC) and columns (6 ft long, $1/8$ in. OD) packed with 10% silicon gum rubber (UCC-W-982) on 60–80 mesh Chromasorb W. was used to perform GLC analyses. Infrared spectra and DTA traces were obtained with a Perkin-Elmer 521 spectrophotometer and a DuPont 990 thermal analyzer, respectively. Capillary melting points are reported and are not corrected.

Determinations of polymer molecular weights ($\bar{M}_n$) in hexafluoroisopropanol were performed by Arro Laboratories, Inc., Joliet, Illinois by using a vapor pressure osmometer.

Poly[ethylene methylene bis(4-phenylcarbamate)] (I)

Polyurethane I was prepared by allowing methylene-p-phenyl diisocyanate to condense with ethylene glycol as described by Lyman.[14]

Reaction of Polyurethane I with Hexamethyldisilazane (II)

A dry Pyrex tube (25 × 2 cm) was charged under nitrogen at Dry Ice–acetone temperature with polymer I (1.5 g, 4.8 mmole) and hexamethyldisilazane (7.74 g, 48.0 mmole). The tube was sealed and heated at 197°C for 21 hr. The tube was cooled in a Dry Ice–acetone bath, opened and the solid removed by filtration and dried *in vacuo*. This material was shown to be 4,4'-diaminodiphenylmethane (III) (0.92 g, 96% yield); acetylation with acetic anhydride afforded 4,4'-bis(acetamido)diphenylmethane,[15] identical in all respects with an authentic sample. The infrared spectrum of the filtrate from the reaction mixture gave a strong absorption at 2290 cm^{-1}, characteristic of an isocyanate moiety. Fractional distillation (Auto Annular Still NFA-200) of this liquid phase from the reaction afforded trimethylisocyanatosilane (IV) (0.82 g, 74.5%), 1,2-bis(trimethylsiloxy)ethane (V) (0.94 g, 95%), hexamethyldisiloxane (VI) (0.40 g, 25%), and bis(trimethylsilyl) carbodiimide (VII) (0.13 g, 15%), which were identi-

fied by comparison with authentic samples.[16-19] Since IV is the most probable limiting reactant involved in the formation of VI and VII as previously discussed, per cent yields of these two compounds are based on the amount of precursor IV present in the reaction mixture.

Poly(ethylene *N,N'*-hexamethylenediamine dicarboxylate) (VIII)

The condensation of ethylene bis(chloroformate) with 1,6-hexane-diamine (XI) gave polyurethane VIII as described by Wittbecker et al.[20]

Reaction of Polyurethane (VIII) with HMDS (II)

A dry Pyrex tube (25 × 2 cm) was charged under nitrogen at Dry Ice–acetone temperatures with polyurethane VIII (1.00 g, 4.35 mmole) and HMDS (6.86 g, 42.5 mmole). The sealed tube was heated at 175°C for 17 hr. The tube was cooled in a Dry Ice–acetone bath, opened and the solid removed by filtration and dried *in vacuo* to afford 0.48 g (78%) of crude IX. Purification was effected by precipitating the polymer from hexafluoroisopropanol (HFIP) with water. The dried sample was identical in all respects to an authentic sample of IX.[11]

The filtrate from the Pyrex tube (8.07 ml) was shown by gas–liquid chromatography (GLC) to be a mixture of trimethylisocyanatosilane (IV) (0.35 g, 69%), hexamethyldisiloxane (VI) (0.12 g, 22%), 1,2-bis(trimethyl-siloxy)ethane (V) (quantitative yield), bis(trimethylsilyl)carbodiimide (VII) (0.083 g, 15%), HMDS and ammonia, which were identified by comparison with the infrared spectrum and GLC retention time of authenti-cally prepared samples. Since IV is the most probable limiting reactant involved in the formation of VI and VII as previously discussed, percentage yields of these two compounds are based on the amount of precursor IV present in the reaction mixture.

Bis(trimethylsilyl)carbodiimide (VII)

A dry Pyrex tube (25 × 2 cm) was charged under nitrogen with tri-methylisocyanatosilane (IV) (1.63 g, 14.1 mmole) and excess HMDS (5.42 g, 33.5 mmole). The sealed tube was heated at 197°C for 21 hr. The cooled tube was opened, and GLC analysis revealed the presence of VII in 12.6% yield. The presence of VII was verified by comparing its retention time with that of an authentic sample[19] of VII.

Polyhexamethyleneurea (IX) from the Reaction of 1,6-Hexanediamine (XI) with Trimethylisocyanatosilane (IV)

A dry Pyrex tube (25 × 2 cm) was charged under nitrogen at Dry Ice–acetone temperature with 1,6-hexanediamine (XI), (0.88 g, 7.57 mmole) and trimethylisocyanatosilane (IV) (1.75 g., 15.19 mmole). The sealed tube was heated at 175°C for 17 hr. The tube was cooled in a Dry Ice–acetone bath, opened, and the solid removed by filtration and dried *in vacuo* to afford 1.06 g (98%) of crude IX. Purification was effected by precipitat-

ing the polymer from HFIP with water. The dried sample ($M_n = 2460$ in HFIP) was identical in all respects to an authentic sample of polyhexamethyleneurea (IX).[11]

The filtrate from the Pyrex tube (1.30 ml) was shown by GLC to be a mixture of five components: trimethylisocyanatosilane (IV) (0.65 g), HMDS (0.32 g), hexamethyldisiloxane (VI) (0.11 g), a trace amount of bis(trimethylsilyl) carbodiimide (VII), and ammonia. Each component was identified by comparison with the infrared spectrum and GLC retention time of authentically prepared samples.

Polyhexamethyleneurea (IX) from the Reaction of 1,1'-Hexamethylenediurea (XII) with HMDS

A dry Pyrex tube was charged with diurea XII (0.46 g, 2.27 mmole) and HMDS (2.32 g, 14.37 mmole) and subjected to the conditions as described above. The solid was removed by filtration and dried *in vacuo* to afford 0.19 g (59%) of crude IX. Purification was effected as described above. The dried sample ($\bar{M}_n = 1620$ in HFIP) was identical in all respects to an authentic sample of polyurea (IX).

The filtrate (2.9 ml) was shown by GLC to contain: trimethylisocyanatosilane (IV) (0.38 g), HMDS (1.70 g), hexamethyldisiloxane (VI) (0.18 g), a trace amount of bis(trimethylsilyl) carbodiimide (VII), and ammonia. Each component was identical with the corresponding authentic samples. When the filtrate was heated to reflux with 10 ml of ethanol for 30 min, a white solid was formed. After being dried *in vacuo*, this material was shown to be unchanged XII (0.15 g, 33.3%).

1,1'-Hexamethylenediurea (XII)

A solution of 0.32 g (2.75 mmole) of XI in 20 ml of dry benzene was added to a stirred solution of 0.63 g (5.50 mmole) of trimethylisocyanatosilane (IV) in 25 ml of dry benzene. The mixture was heated at reflux for for 2 hr; 10 ml of ethanol was added, and reflux continued for an additional 30 min. The resulting white solid was removed by filtration and recrystallized from 20 ml of ethanol to afford 0.44 g (79%) of pure VIII, mp 205–206°C (lit.[21] mp 205–206°C).

Thermolysis of 1,1'-Hexamethylenediurea (XII) in Toluene

A Pyrex tube was charged with XII (0.12 g, 0.54 mmole) and 3.0 ml of toluene and sealed as described above. The tube was heated at 175°C for 17 hr. The solid was removed by filtration and dried *in vacuo*, 0.10 g. The infrared spectrum of this product differed significantly from that of polyurea IX and of starting material XII, showing relatively strong absorption at 1700 cm^{-1} not present in these compounds. The DTA trace of the thermolysis product also showed endothermic peaks from 100 to 275°C not present in IX. Also, the authentic polyurea IX had a prominent endotherm at 280°C which was absent in the thermolysis product. Repetition of this experiment at 206°C gave essentially the same results.

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